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N63-11616
Code 1
24 pages

TECHNICAL NOTE

D-1533

RELATIVE IGNITABILITY OF TYPICAL SOLID PROPELLANTS

WITH CHLORINE TRIFLUORIDE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON January 1963

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SUMMARY

Ignition delays were measured after exposing samples of solid propellants and their components to the hypergolic fluid, chlorine trifluoride (ClF_3), in both the liquid and the gas phases. A comparison of these ignition-delay data serves as a measure of the relative reactivity of these propellant compositions with ClF_3. The gas-phase studies showed that the ignition delay varied exponentially with ClF_3 pressure and approached a limit of less than 50 milliseconds at 14 pounds per square inch absolute, the maximum pressure permitted by the experimental apparatus. The gas-phase studies also revealed that the reactivity of the propellant formulation was greatly affected by changes in concentrations of the dispersed solid components (ammonium perchlorate and aluminum) of the propellant. After reaching a minimum point, the ignition delay of the propellant increased with an increase in the concentration of the ammonium perchlorate component; with an increase in the concentration of the aluminum component, the ignition delay was decreased. All the propellant formulations were extremely reactive with liquid ClF_3 and had ignition delays of less than 3 milliseconds.

INTRODUCTION

Recently, the feasibility of igniting solid-propellant rocket motors with hypergolic fluid chemicals was demonstrated (refs. 1 and 2). This method of ignition offers the possibility for reigniting solid-propellant motors during space missions. In reference 1 it was reported that of the three interhalogen compounds that were used successfully to ignite motors containing composite and double-base propellants, chlorine trifluoride (ClF_3) was the most effective. Consequently, a further investigation into the process of igniting a solid propellant with ClF_3 was undertaken. The objective of this investigation was to determine which of the principal components (fuel, oxidizer, or metal additive) of the propellant actually reacts with ClF_3 to cause ignition and also to determine what effect the other components have on the ignition delay of the process.

This report is concerned with some of the initial results of this study. Samples of various propellant formulations and their components were rapidly

exposed to ClF_3 in the liquid and the gas phases. Ignition delays were obtained from measurements of pressure rise and light emission.

APPARATUS AND PROCEDURE

Gas Phase

The apparatus used for the gas-phase studies is shown in figure 1. It consisted of two 2-inch-diameter by 6-inch-long stainless-steel chambers separated by a thin aluminum diaphragm. The gaseous ClF_3 was contained in one chamber and the test sample with its associated instrumentation was mounted in the other chamber. The mechanism for cutting the separation diaphragm consisted of a circular knife attached to a movable piston that was built into the sample chamber. A small aluminum burst diaphragm was located at the other end of the sample chamber. The entire apparatus was attached to an evacuated tank, which received the hot gaseous contents of the apparatus when the burst diaphragm was ruptured.

The following test procedure was used for each sample: After the apparatus had been assembled with the test specimen and diaphragms in place, it was evacuated. Then gaseous ClF_3 from a storage tank containing 99.7-percent-pure ClF_3 was bled into the ClF_3 chamber to a desired pressure. High-pressure (1000 lb/sq in. gage) nitrogen was forced into the cutter assembly and caused the knife to cut the aluminum diaphragm. The gaseous ClF_3 pushed the cut diaphragm aside and diffused down to the test specimen; hypergolic ignition and combustion caused the chamber pressure to rise and resulted in the rupture of the burst diaphragm at 200 pounds per square inch absolute. The actual ClF_3 pressure, to which the sample was exposed, was determined by previously calibrating the apparatus with air.

Liquid Phase

The apparatus used for the liquid-phase studies (fig. 1(b)) was similar in design and operational principles to the gas-phase apparatus and consisted of a liquid ClF_3 chamber (1-in. diam. by $1\frac{1}{2}$-in. length) located above and separated by an aluminum diaphragm from the test sample chamber (1-in. diam. by 2-in. length). The mechanism for cutting the diaphragm was a plunger with attached knife blades located in the ClF_3 chamber. An aluminum burst diaphragm was located at the bottom of the sample chamber.

After the specimen with its associated instrumentation was placed in the sample chamber, the apparatus was assembled with the liquid ClF_3 transfer bottle in place. The apparatus was evacuated, and then the sample chamber was pressurized with 30-pound-per-square-inch-absolute nitrogen gas to prevent the liquid ClF_3 from vaporizing as it entered the sample chamber when the aluminum diaphragm was cut. Five cubic centimeters of liquid ClF_3 were transferred to the upper chamber from the transfer bottle and pressurized to 40 pounds per square inch gage with helium. High-pressure nitrogen was forced into the cutter assembly and caused the knife-edge plunger to shear the aluminum diaphragm. The liquid ClF_3 under pressure dropped and completely covered the test sample.

After hypergolic ignition had occurred, the pressure of the combustion gases caused the burst diaphragm to rupture, and the hot gaseous products were dumped into the evacuated tank.

INSTRUMENTATION

Pressure, temperature, and light intensity were the parameters measured. Strain-gage-type pressure pickups (0 to 100 lb/sq in. abs and 0 to 300 lb/sq in. abs) were used to measure pressure rise. Iron-constantan (0° to 200° F) and Chromel-Alumel (0° to 2000° F) thermocouples were used to measure temperature rise. Number 931A photomultiplier tubes (with a range of 3000 to 5000 A) with appropriate circuitry measured the intensity of the light emitted from the ignition reaction. The outputs from all these instruments were channeled into a direct-recording oscillograph.

The positions and types of instrument used for the gas- and the liquid-phase apparatus are depicted in figure 1. All the instruments were placed as close to the test specimen as possible. The thermocouple junctions touched the surface of the sample and the photomultiplier-tube windows viewed a sample surface area of approximately 3/16-inch diameter.

Typical recorder traces for both the gas- and the liquid-phase studies are presented in figure 2. Initially, the pressure instruments measured the pressure of the sample chamber; then, when the aluminum diaphragm was cut, they indicated the resultant pressure of the ClF_3 to which the sample was exposed. As ignition and combustion proceeded, the pressure rose until the rupture of the burst diaphragm caused the pressure to decline. The surface temperatures of the sample did not begin to rise appreciably until ignition and combustion were well underway, and they reached their maximum values shortly after the sample had completely burned. A part of the initial temperature rise for all the thermocouple traces was due to the reaction of ClF_3 with the thermocouple junction. The light intensity built up to an approximately constant level until the entire sample was consumed and then dropped rapidly to zero. The ignition delay was considered to be the time interval between contact of ClF_3 with the test sample, as indicated by the step in the pressure pickup trace, and the first indication of continuous light emission from the photomultiplier tube.

For the gas-phase studies (fig. 2(a)), the sample chamber was initially evacuated. The time for the ClF_3 to diffuse from the diaphragm to the sample (a distance of approximately 5 in.) was imperceptible, as shown by a comparison of the first inflection points of pressure traces 1 and 2. The ignition delay was measured by using pressure pickup 2, which was adjacent to the sample, and the average of the two photomultiplier-tube readings.

TEST SPECIMENS

The particle sizes of the components and the compositions of the various propellant mixtures investigated are listed in table I. Most of the formulations were made at the Lewis Center; however, a few commercial formulations

were investigated for comparison. The ammonium perchlorate (AP) and aluminum (Al) powders were placed in aluminum trays for study. The binders and propellant samples were studied as slabs of the following dimensions: 1/2 by 1/8 by 1 inch for gas studies and 1/2 by 1/2 by 1/8 inch for liquid studies. All slab samples had freshly cut surfaces.

Of the specimens listed in table I, three of the polyurethane (PU) formulations were prepared to permit comparison of ignition behavior with a constant ratio of particle area to binder area. These compositions were as follows:

Ingredient	Composition, weight percent, for formulation -		
	I	II	III
PU	70.4	70.0	69.8
AP	29.6	----	14.4
Al	----	30.0	15.8

It was estimated, on the basis of a cubic array of spherical particles of uniform 7-micron-diameter Al and 9-micron-diameter AP, that the total particle surface area was 1000 square centimeters per cubic centimeter of composition, and that approximately one-third of the exposed (cut) surface was PU.

RESULTS AND DISCUSSION

Gas-Phase Studies

As a working hypothesis, the ignition of a composite propellant with hypergolic fluids was attributed principally to a reaction between a strong oxidizing agent such as ClF_3 and the fuel binder component of the propellant; however, preliminary experiments showed that powdered ammonium perchlorate (AP) and aluminum (Al) can also react vigorously with ClF_3.

Dispersed solid components of propellants. - Ignition delay is plotted against ClF_3 pressure for these components in figure 3(a). The curves were fitted to the data by the method of least squares (solid line) and extrapolation (dashed line) to a limiting ClF_3 pressure. In each case, the ignition delay increased with decreasing ClF_3 pressure until a pressure was reached, below which there was no ignition. The relative positions of these curves for AP and Al are, of course, dependent on the particle size of these powders; however, these are the particle sizes that were incorporated into the subsequent propellant formulations. The ignition of these powdered components cannot be compared with the following fuel-binder ignition data because of the surface-area differences, and the individual reaction of these ingredients with ClF_3 is not indicative of how they might react if they were imbedded in the surface of a blended propellant formulation.

Fuel-binder components of propellants. - Ignition delay is plotted against ClF_3 pressure for polyurethane (PU) and polysulfide (PS) fuel binders in figure 3(b). Again, the ignition delay increased with decreasing ClF_3 pressure until a pressure was reached, below which there was no ignition. Extrapolation of the curves to 25 pounds per square inch absolute, the vapor pressure of ClF_3 at room temperature, would indicate ignition delays of the order of a few milliseconds. Polybutadiene acrylic acid (PBAA) fuel binder was also investigated and was difficult to ignite. At the same ClF_3 pressure, the ignition delay varied from long to short periods of time. The marginal ignitability of PBAA persisted down to a pressure of 10 pounds per square inch absolute, below which no ignition would occur. In a comparison of the data for the fuel binders, the order of decreasing reactivity was PS, PU, and PBAA. If the actual surface area of the samples of the various polymers were constant, then the shapes of the curves in figure 3(b) would indicate that the reactions were of higher than first order with respect to ClF_3.

It should be noted that the ignition-delay data and the minimum ClF_3 pressure were functions of the apparatus and the sample geometry. When the ratio of surface area to apparatus volume was halved (by using 1/2- by 1/2- by 1/8-in. test samples), the ignition-delay curve was shifted slightly to the right of the original position, which was indicative of the change in reaction rate associated with the decrease in sample size.

Polyurethane - ammonium perchlorate compositions. - In figure 3(c), plots of ignition delay against ClF_3 gas pressure for combinations of PU with AP are compared with data for PU alone. The addition of 29.6 percent AP to PU decreased the minimum ClF_3 pressure required for ignition, while the addition of 60 and 80 percent AP to PU increased the pressure to a value higher than that for the PU alone. This indication of a minimum in the ignition delay can be explained by a two-step reaction: first, the reaction of ClF_3 with PU to raise the temperature from the ambient temperature T_0 to T_1, a temperature at which AP has a significant rate of decomposition; and second, a reaction between PU and the AP decomposition products to raise the temperature to the ignition temperature T_{ig}. If the fuel and oxidizer concentrations are assumed proportional to surface areas, these processes may be expressed as follows:

$$\tau = \tau_1 + \tau_2 \tag{1}$$

$$\tau_1 = \frac{k_1}{(S_b)^w (ClF_3)^x} \tag{2}$$

$$\tau_2 = \frac{k_2}{(S_b)^y (S_o)^z} \tag{3}$$

where τ_1 is the time required for the binder-ClF_3 reaction to raise the temperature from T_0 to T_1; τ_2 is the time required for the binder-AP reaction to raise the temperature from T_1 to T_{ig}; S_b is the fraction of the surface which was the exposed fuel binder; S_o is the fraction of the surface which was the exposed AP; (ClF_3) is the concentration of ClF_3; w, x, y, and z are exponents determined by the order of the rate equation; and k_1 and k_2 are proportionality constants.

For single ingredients, only equation (2) applies, but for combinations of fuel and oxidizer, the value of τ_2 and therefore τ will be a minimum at some particular combination of S_b and S_o, as suggested by the data, since $S_b = 1 - S_o$. These equations obviously ignore the effect of composition on heat capacity and thermal conductivity and assume that the constants k_1 and k_2 do not vary with time and hence that the temperature is nearly constant until ignition occurs.

Polyurethane-aluminum compositions. - The addition of 30-percent-Al powder to PU binder increased the ignition delay over that of the binder alone and increased the minimum ClF_3 pressure for ignition (fig. 3(d)). The figure shows that 30 percent Al in the PU binder, of which two-thirds of the exposed surface was PU, required for ignition a ClF_3 pressure three times that required by the PU binder alone. The ClF_3 appeared to react preferentially with the fuel binder, rather than with the Al component of the mixture; thus, the reaction of ClF_3 with fuel binder seemed to be the first step in the ignition process, as postulated in the previous section.

Polyurethane - aluminum - ammonium perchlorate compositions. - Comparison of figures 3(c) to (e) showed that the addition of aluminum to propellant (PU and AP mixtures) gave (with the exception of 29.6 percent AP in PU) shorter ignition delays and a lower ClF_3 pressure limit for ignition than PU alone, PU plus Al, or PU plus AP. Apparently, the reaction of decomposing AP with Al contributes significantly to ignition along with the process previously mentioned. The commercial propellant containing 15 percent Al and 60 percent AP was more difficult to ignite than the 15.8-percent-Al and 14.4-percent-AP propellant, presumably in agreement with the previously discussed minimum in ignition delay as a function of AP concentration.

Effect of equal binder surface area on polyurethane propellants. - In figure 3(f) are plotted together data for compositions I, II, and III, the PU formulations that were designed to give approximately the same effective binder surface area for reaction; that is, the ratio of binder area to particle area in the exposed surface area was held constant for all formulations, while the composition of the particles was varied. In order of increasing ignition delay, these mixtures were: 15.8 percent Al - 14.4 percent AP in the binder, 29.6 percent AP in the binder, and 30 percent Al in the binder. Thus, by removing the complication of a varying effective binder surface area, the conclusions previously drawn concerning the effect of the AP and Al addition on the reactivity of binder were reemphasized.

Although the reactivity of the propellant appeared not to depend solely on one component, it can be concluded from all the experimental data for the PU

formulations that the addition of practical quantities (greater than 60 percent) of AP to the propellant increased the ignition delay, while the addition of Al decreased the ignition delay of the propellant mixtures.

Polysulfide propellant compositions. - The PS propellant formulations (fig. 3(g)) were so reactive with ClF_3 that the differences between ignition-delay curves were not very large. When appreciable amounts (greater than 60 percent) of AP were blended with PS binder, the resulting propellant was less reactive with ClF_3 than fuel binder alone. The addition of aluminum to the propellant mixture, however, increased the reactivity and thus decreased the ignition delay. Therefore, the results for the PS propellant were similar to those for the PU propellant.

Polybutadiene acrylic acid propellant compositions. - Generally, the PBAA propellant formulations were difficult to ignite; when ignition did occur, it was very erratic. The marginal ignition of the PBAA fuel binder and the commercial PBAA plus AP mixture resulted in data that were too scattered to be fitted to curves. Two NASA formulations of 30 percent Al in PBAA and 60 percent AP in PBAA were unignitable. Thus, this scatter in the ignition-delay data prohibited observing the effect of the AP addition to the PBAA binder. When Al was added to the propellant mixture, it increased the reactivity of the propellant and decreased the scatter in the ignition-delay data (fig. 3(h)). All PBAA formulations were unignitable below a ClF_3 pressure of 9 pounds per square inch absolute.

Double-base propellants. - The double-base propellant was unignitable with gaseous ClF_3 at the highest ClF_3 pressures permitted in the test apparatus.

Liquid-Phase Studies

The results of the liquid-phase studies are presented in table II. All the composite propellant formulations were ignited with liquid ClF_3. Even the double-base propellant was ignited with liquid ClF_3, whereas it was unignitable with gaseous ClF_3. The ignition delays were all less than 3 milliseconds; because of the very short ignition delays, there was no evidence of the effect of the AP and the Al powders, as in the case of the gas-phase studies.

A clear relation between the gas- and liquid-phase studies is not evident from these preliminary investigations. If the ignition mechanism were the same for both phases, much shorter delays (of the order of microseconds or less) would be expected for the very high concentration of ClF_3 in the liquid phase, as compared with the gas phase. Since the liquid-phase delays are of the same order of magnitude as the gas-phase delays would appear to be if the gas-data curves were extrapolated to 25 pounds per square inch absolute (the vapor pressure above liquid ClF_3 at room temperature), two explanations are possible: Either the ignition mechanisms for both phases are different or the ignition with liquid ClF_3 is actually due to a gas-phase mechanism resulting from a phase change. Further investigation is necessary to determine which explanation is valid.

SUMMARY OF RESULTS

Ignition delays were measured after exposing samples of solid propellants and their components to the hypergolic fluid, chlorine trifluoride (ClF_3), in both the liquid and the gas phases. A comparison of these ignition-delay data served as a measure of the relative reactivity of these materials with ClF_3.

The following observations were drawn from an analysis of the gas-phase ignition-delay data:

1. The ignition delays for most test samples decreased exponentially as the ClF_3 gas pressure increased and approached a limit of less than 50 milliseconds at 14 pounds per square inch absolute ClF_3 (the maximum pressure limit of the experimental apparatus).

2. For each test sample there was a lower ClF_3 pressure limit, below which no ignition occurred.

3. All the principal components (fuel binder, ammonium perchlorate oxidizer, and aluminum metal additive) of composite propellants reacted individually with gaseous ClF_3.

4. The relative ignitabilities of the fuel binders and their corresponding propellants in decreasing order were polysulfide, polyurethane, and polybutadiene acrylic acid.

5. The addition of practical quantities (greater than 60 percent) of ammonium perchlorate to a binder decreased the reactivity of the resulting propellant with ClF_3 and thus increased the ignition delay. There was a minimum in ignition delay at lower concentrations of ammonium perchlorate.

6. When aluminum was added to the propellant formulation, the reactivity of the mixture with ClF_3 was greatly increased and the ignition delay was thus markedly decreased.

7. The double-base propellant was unignitable with gaseous ClF_3.

Liquid ClF_3 was very reactive with all the propellants, including the double-base propellant. All the ignition delays were less than 3 milliseconds. The ignition delays of the propellant compositions were so short that the separate effects of the components could not be observed as in the case of the gas-phase studies.

A comparison of the ignition-delay data for liquid and gaseous ClF_3 indicated that either the ignition mechanism for each phase is different or the ignition with liquid ClF_3 is actually due to a gas-phase mechanism resulting from a phase change.

CONCLUDING REMARKS

Inasmuch as this paper is a report of the experimental data to date, the conclusions drawn and the theories offered are necessarily tentative. Further investigation into the process of igniting a solid propellant with chlorine trifluoride is needed to permit proper design of this type of ignition system for specific solid-propellant rocket motors.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, August 30, 1962

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1. Ciepluch, Carl C., Allen, Harrison, Jr., and Fletcher, Edward A.: Ignition of Solid Propellant Rocket Motors by Injection of Hypergolic Fluids. ARS Jour., vol. 31, no. 4, Apr. 1961, pp. 514-518.

2. Priapi, J. J.: Advanced Ignition System for Solid Propellant Rocket Motors. ARS Jour., vol. 31, no. 7, July 1961, pp. 1029-1031.

TABLE I. - FORMULATIONS OF TEST SPECIMENS

(a) NASA propellants

Sample	Binder		Oxidizer		Aluminum	
	Type (a)	Weight percent	Particle size, μ	Weight percent	Particle size, μ	Weight percent
MP-2244	PU	70	----	----	6.92	30
MP-2278	PU	70	8.65	30	----	----
MP-2311	PU	40	8.65	60	----	----
MP-2310	PU	20	8.65	80	----	----
MP-2281	PU	69.8	8.65	14.4	6.65	15.8
MP-2329	PS	40	8.4	60	----	----
MP-2327	PBAA	70	----	----	6.65	30
MP-2328	PBAA	40	8.4	60	----	----

(b) Commercial composite propellants

Sample identification (a)	Binder		Oxidizer				Aluminum	
	Type (a)	Weight percent	Ground		Unground		Particle size, μ	Weight percent
			Particle size, μ	Weight percent	Particle size, μ	Weight percent		
PS + AP	PS	28.48	9	21.46	195	50.06	--	--
PS + AP + Al	PS	26	8	39.60	225	32.40	25	2
PU + AP + Al	PU	25	9	18	195	42	25	15
PBAA + AP	PBAA	17	9	58.10	297	24.90	--	--
PBAA + AP + Al	PBAA	17.60	9	44	195	26.40	10	12

(c) Commercial double-base propellant

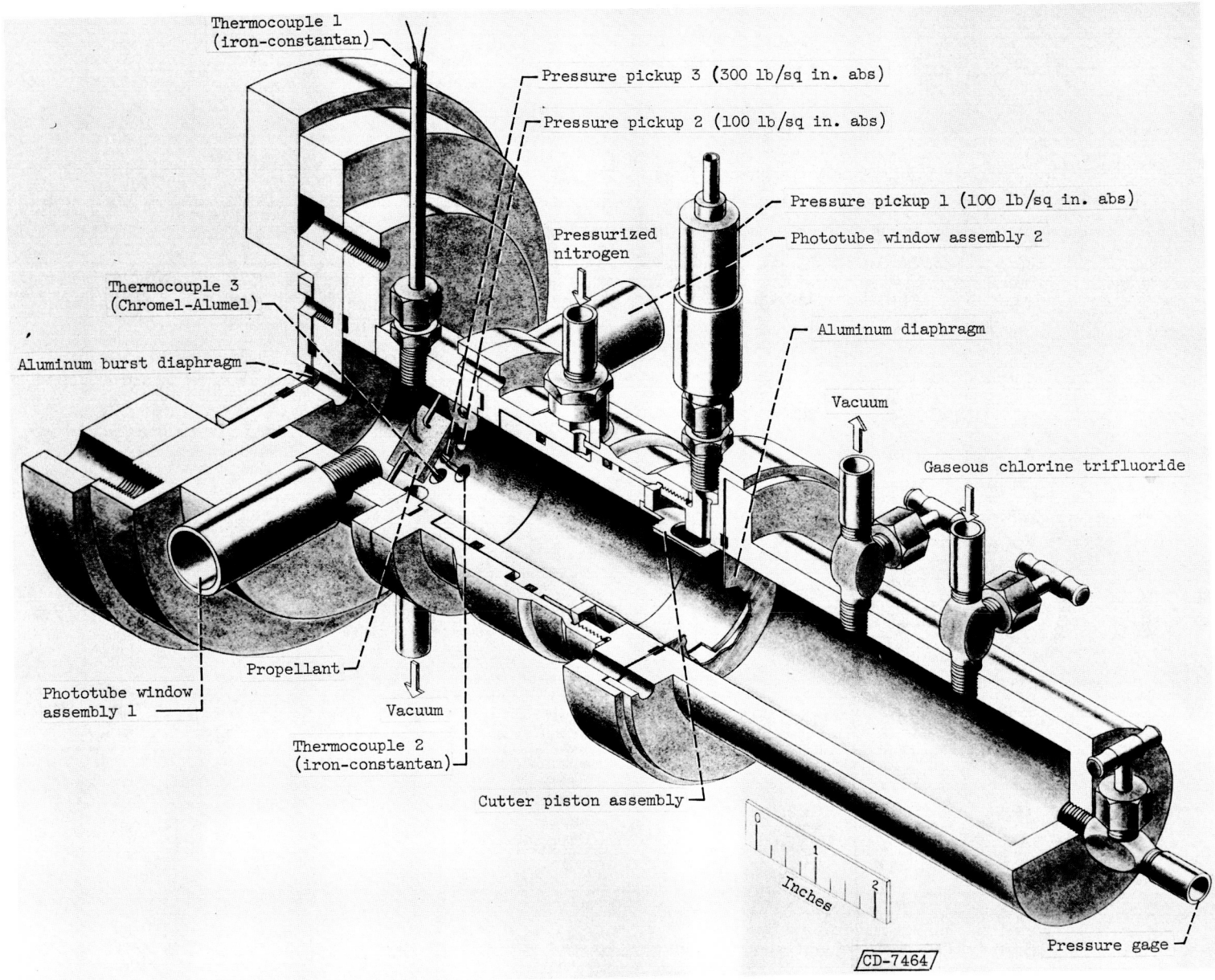
Component	Composition, weight percent
Nitrocellulose	53.26
Nitroglycerine	35.96
Triacetin	8.81
2-Nitrodiphenylamine	1.63

[a]Polyurethane, PU; polysulfide, PS; polybutadiene acrylic acid, PBAA; ammonium perchlorate, AP; and aluminum, Al.

TABLE II. - IGNITION DELAYS OF LIQUID CHLORINE TRIFLUORIDE WITH SOLID PROPELLANTS

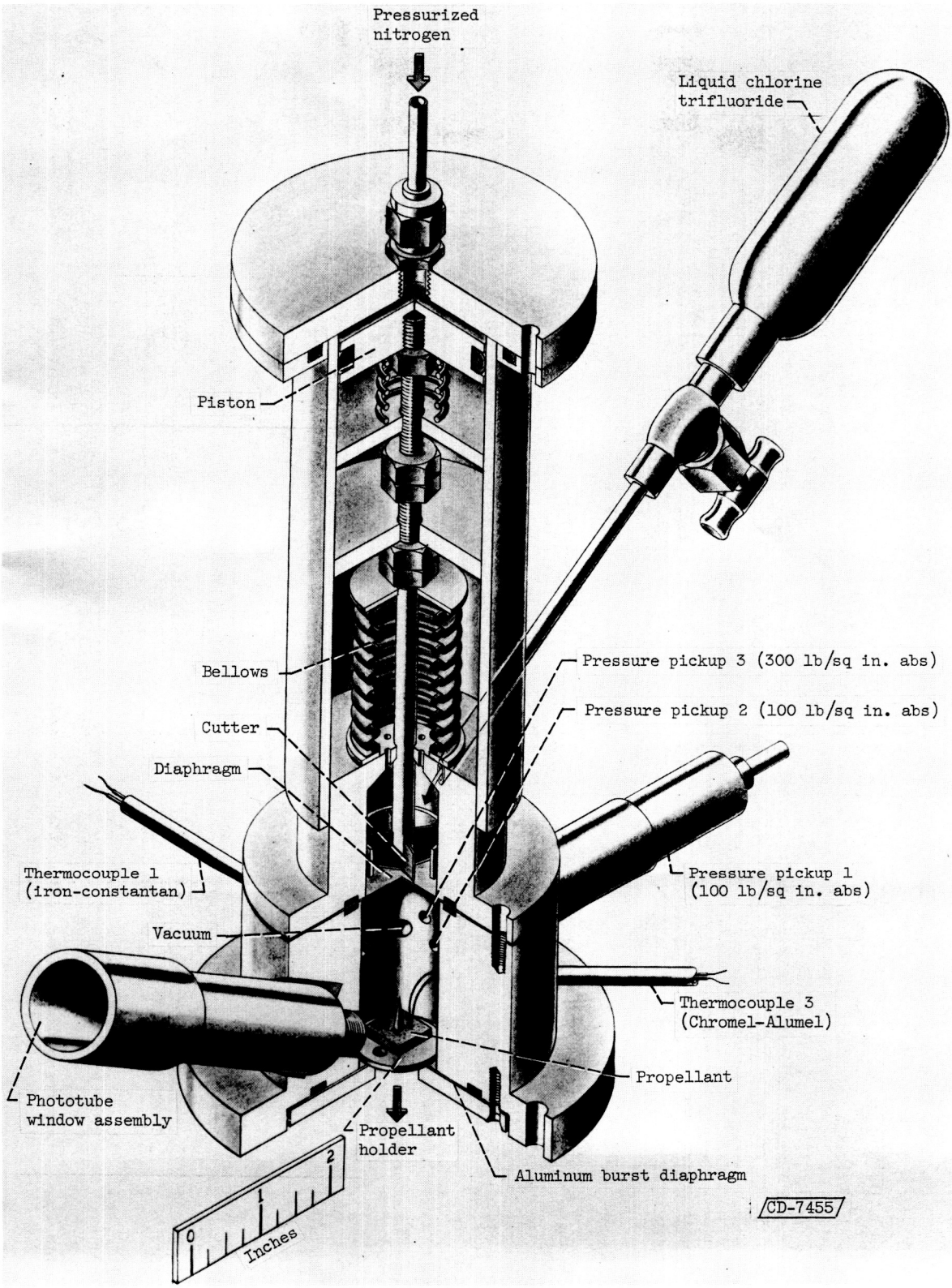
Sample identification (a)	Source	Ignition delay, msec
PU binder	NASA; MP 2303	2.0
PS binder	NASA; MP 1988	1.0
PBAA binder	NASA; MP 2013	1.0
PS + AP	Commercial composite	1.2
PBAA + AP	↓	2.0
PU + AP + Al	↓	1.8
PS + AP + Al	↓	1.0
PBAA + AP + Al	↓	3.0
Double base	Commercial double base	3.0

[a]Polyurethane, PU; polysulfide, PS; polybutadiene acrylic acid, PBAA; ammonium perchlorate, AP; and aluminum, Al.



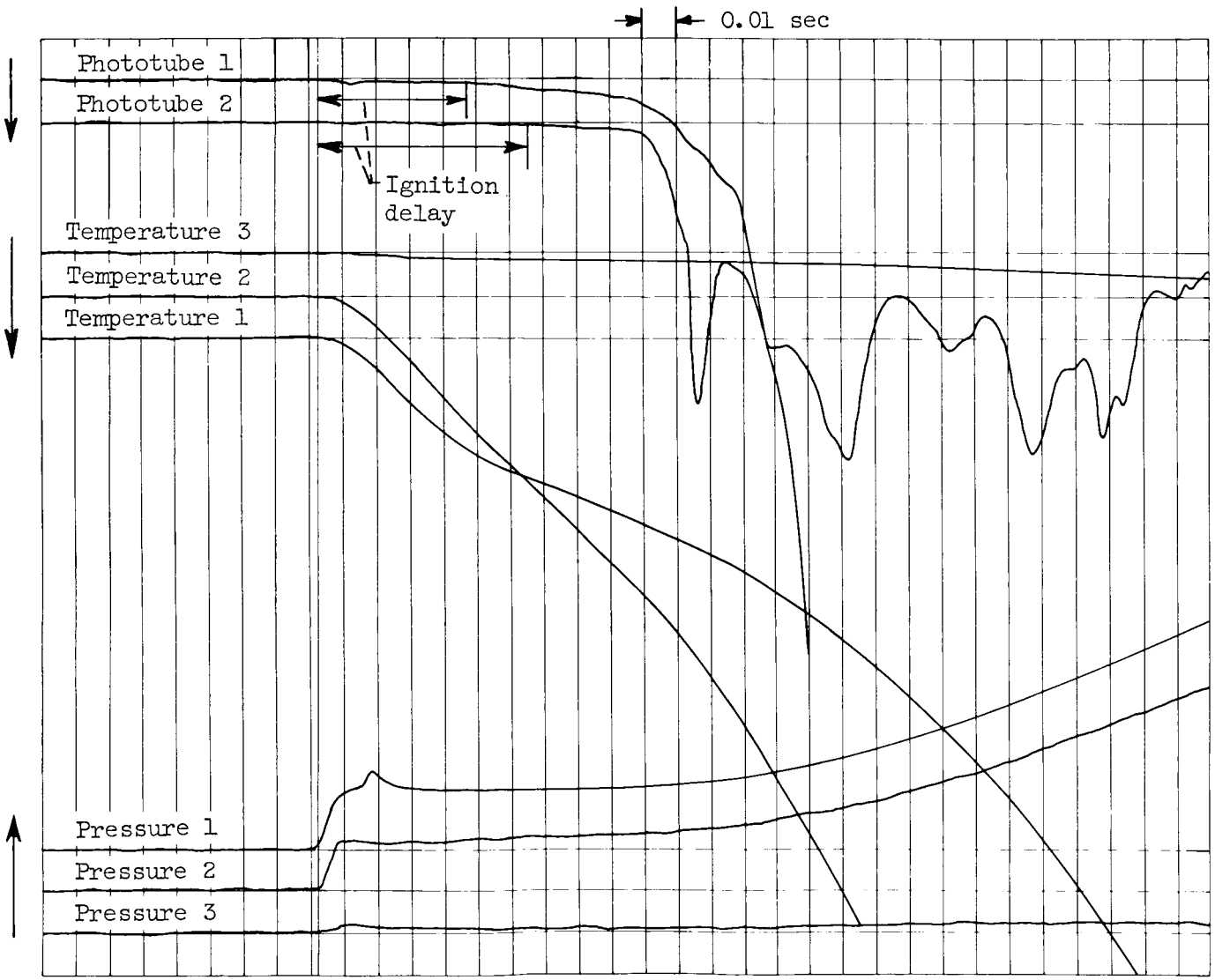
(a) Gaseous chlorine trifluoride study.

Figure 1. - Solid-propellant ignition apparatus.



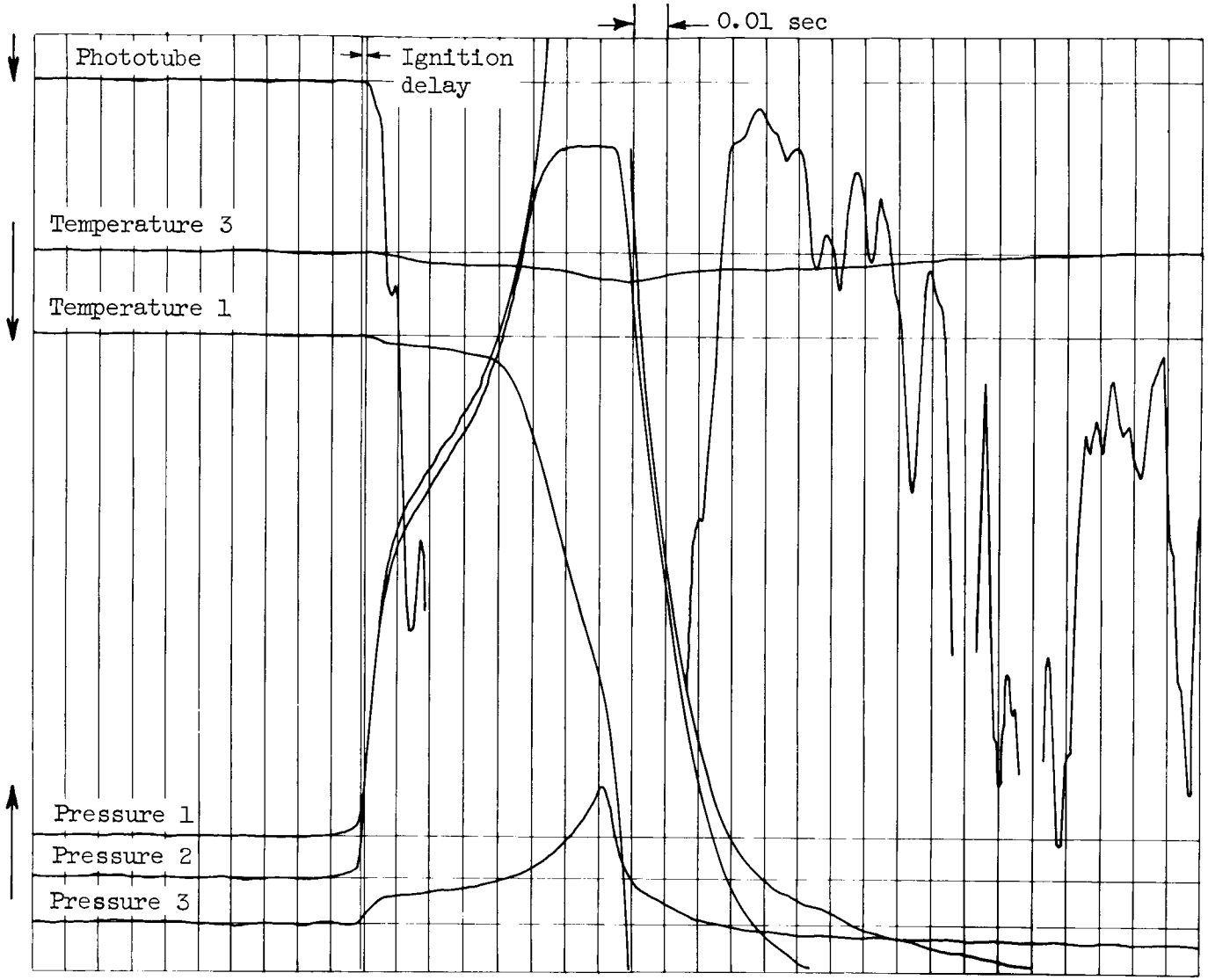
(b) Liquid chlorine trifluoride study.

Figure 1. - Concluded. Solid-propellant ignition apparatus.



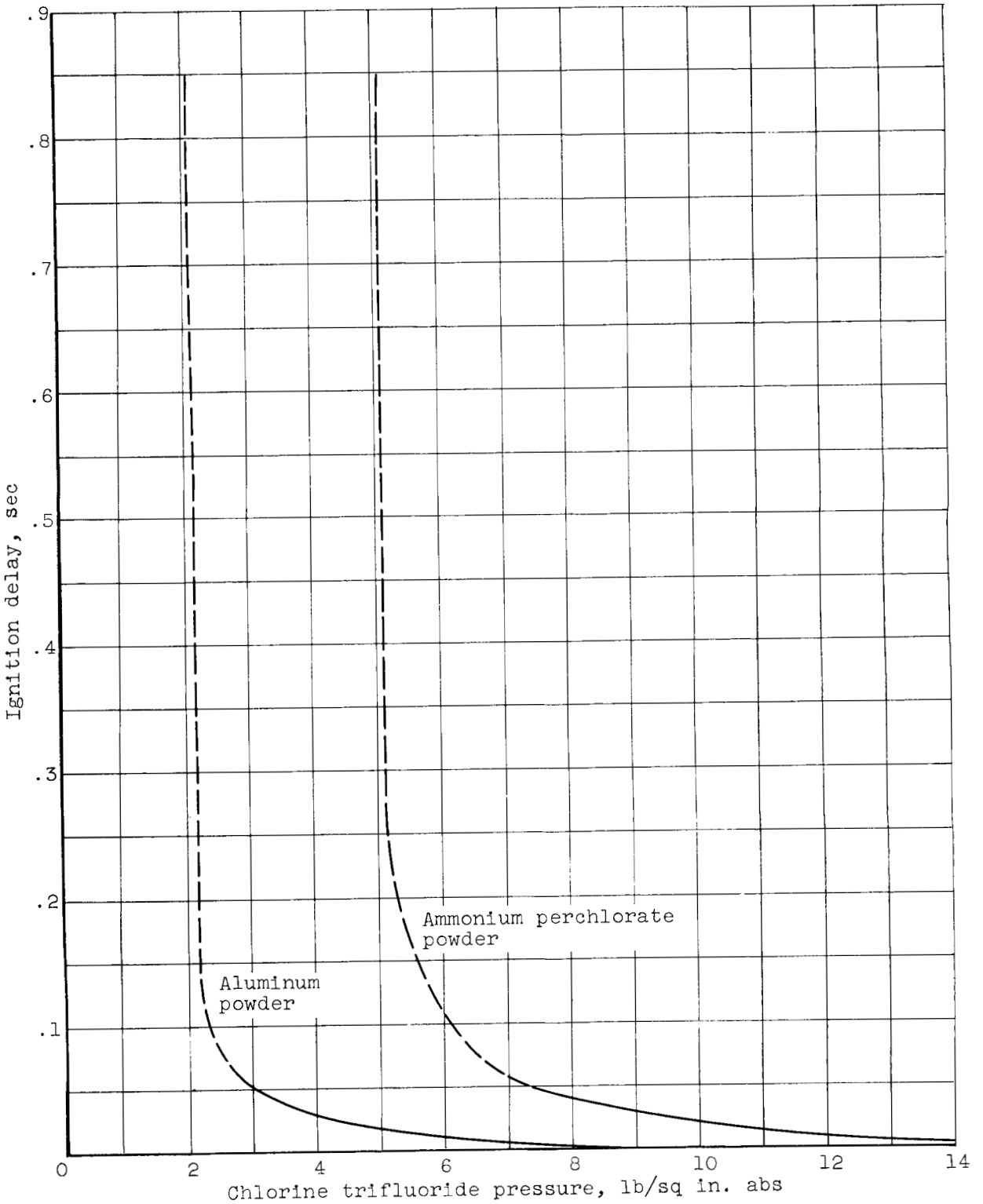
(a) Gas-phase study.

Figure 2. - Oscillograph traces of light-emission, temperature, and pressure changes during ignition of typical solid propellant.



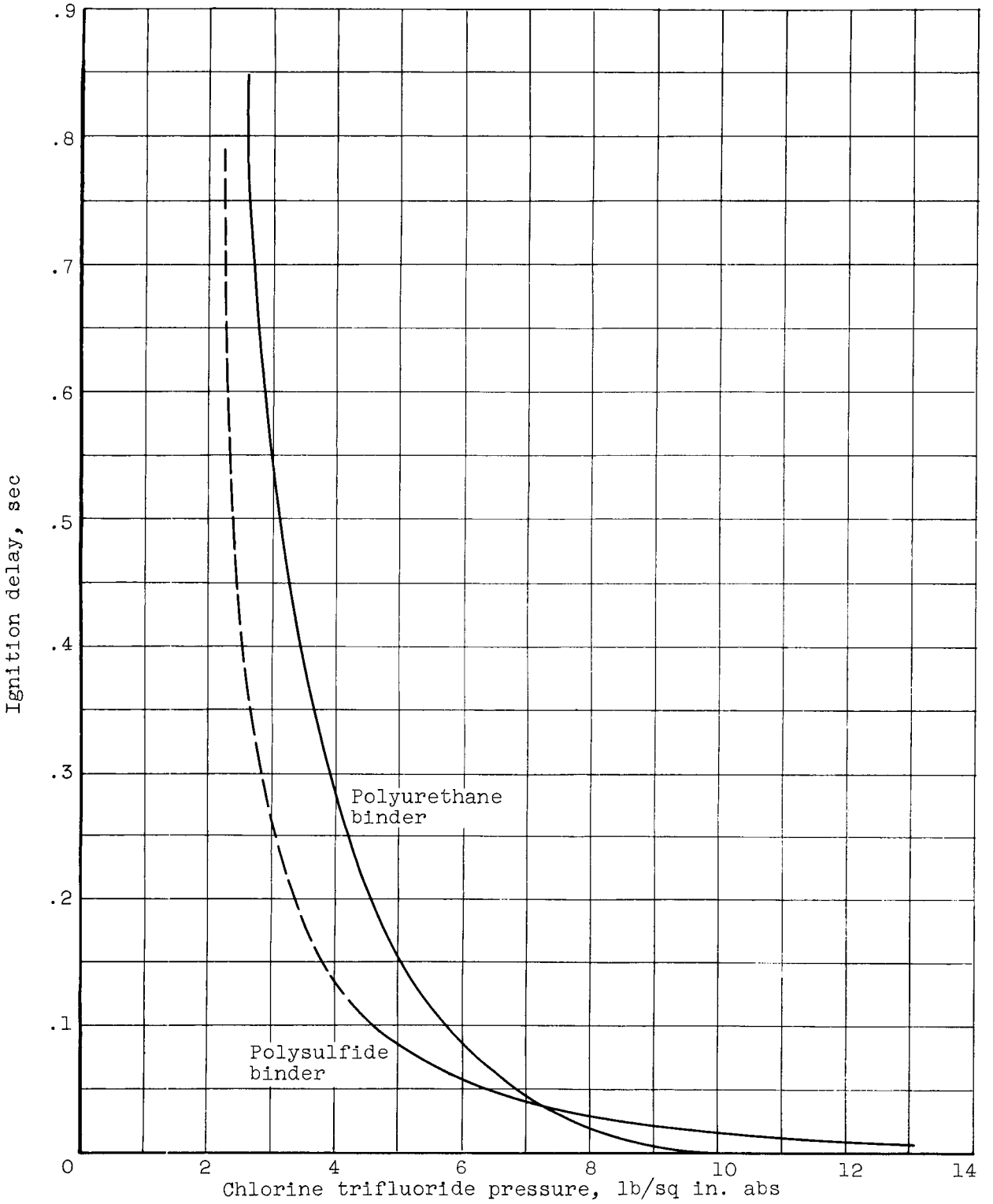
(b) Liquid-phase study.

Figure 2. - Concluded. Oscillograph traces of light-emission, temperature, and pressure changes during ignition of typical solid propellant.



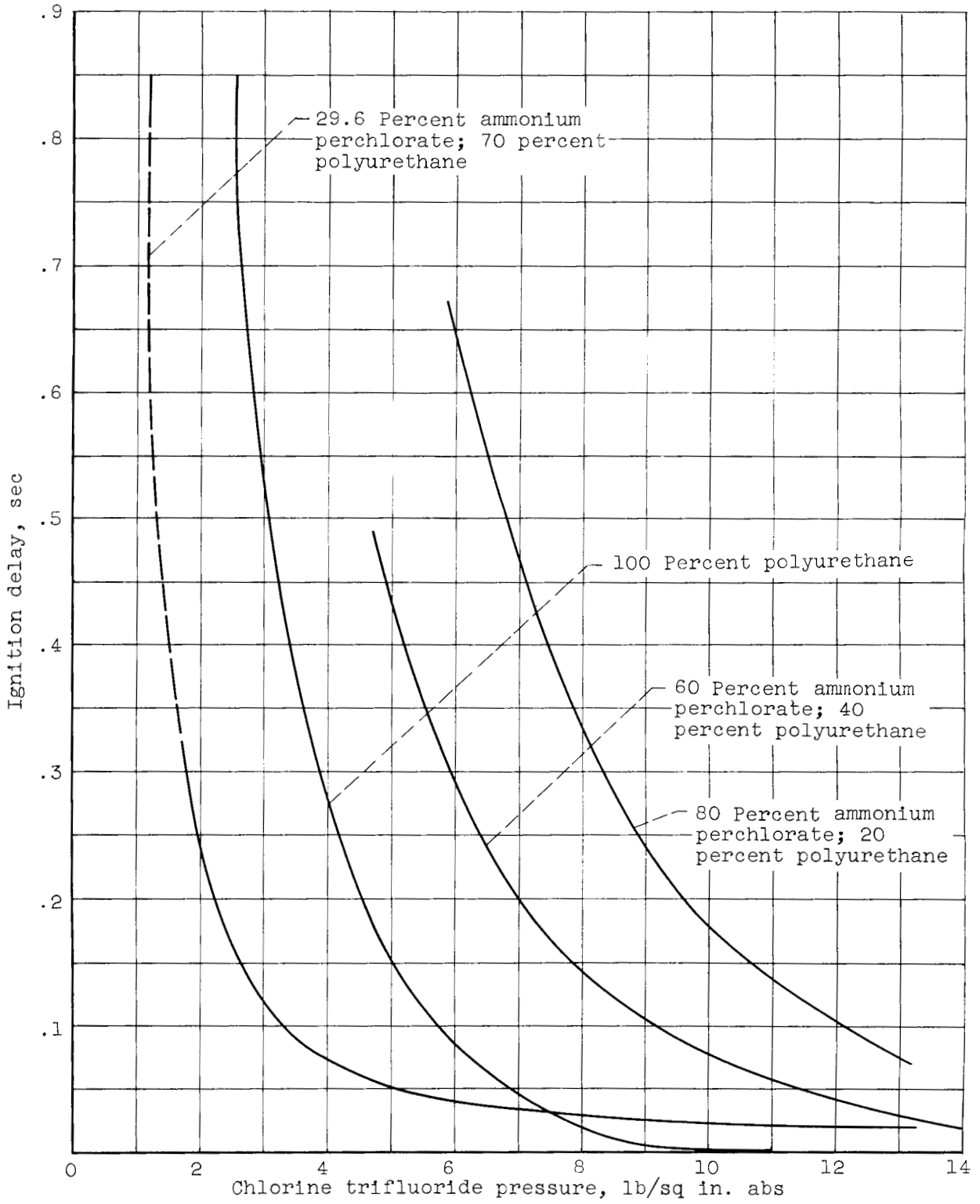
(a) Dispersed solids of propellants.

Figure 3. - Ignition delay.



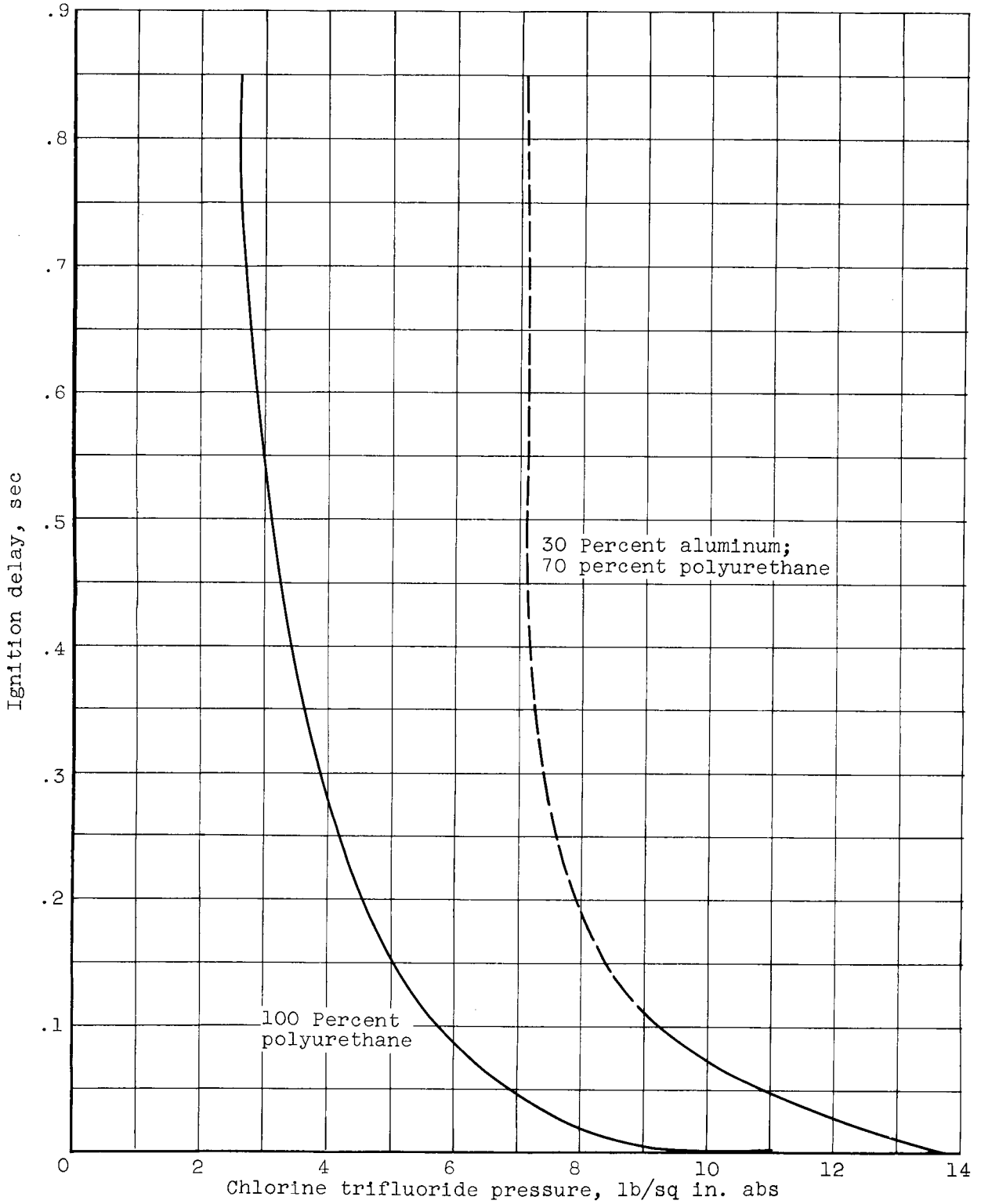
(b) Fuel binders of propellants.

Figure 3. - Continued. Ignition delay.



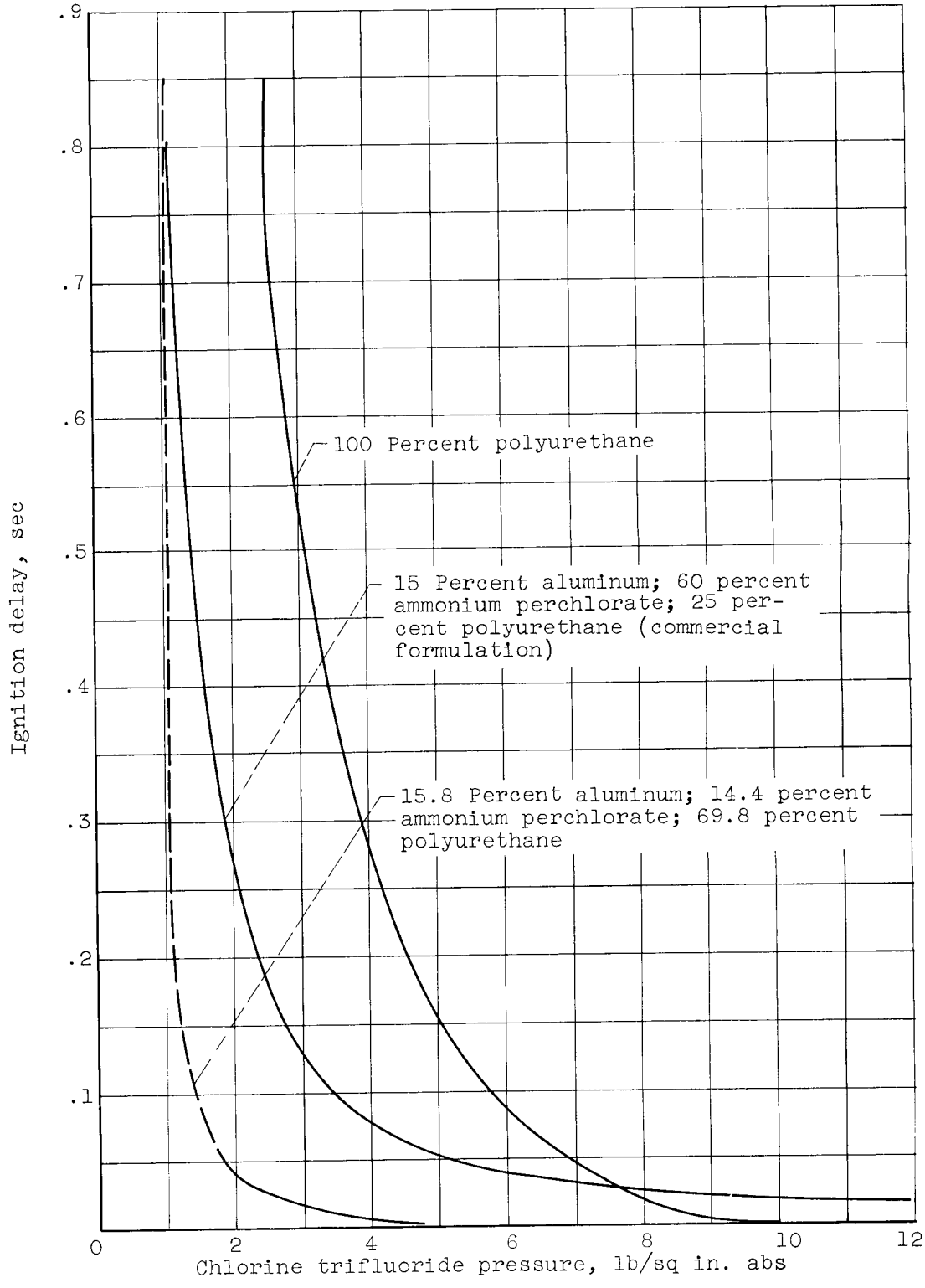
(c) Effect of ammonium perchlorate addition to polyurethane binder.

Figure 3. - Continued. Ignition delay.



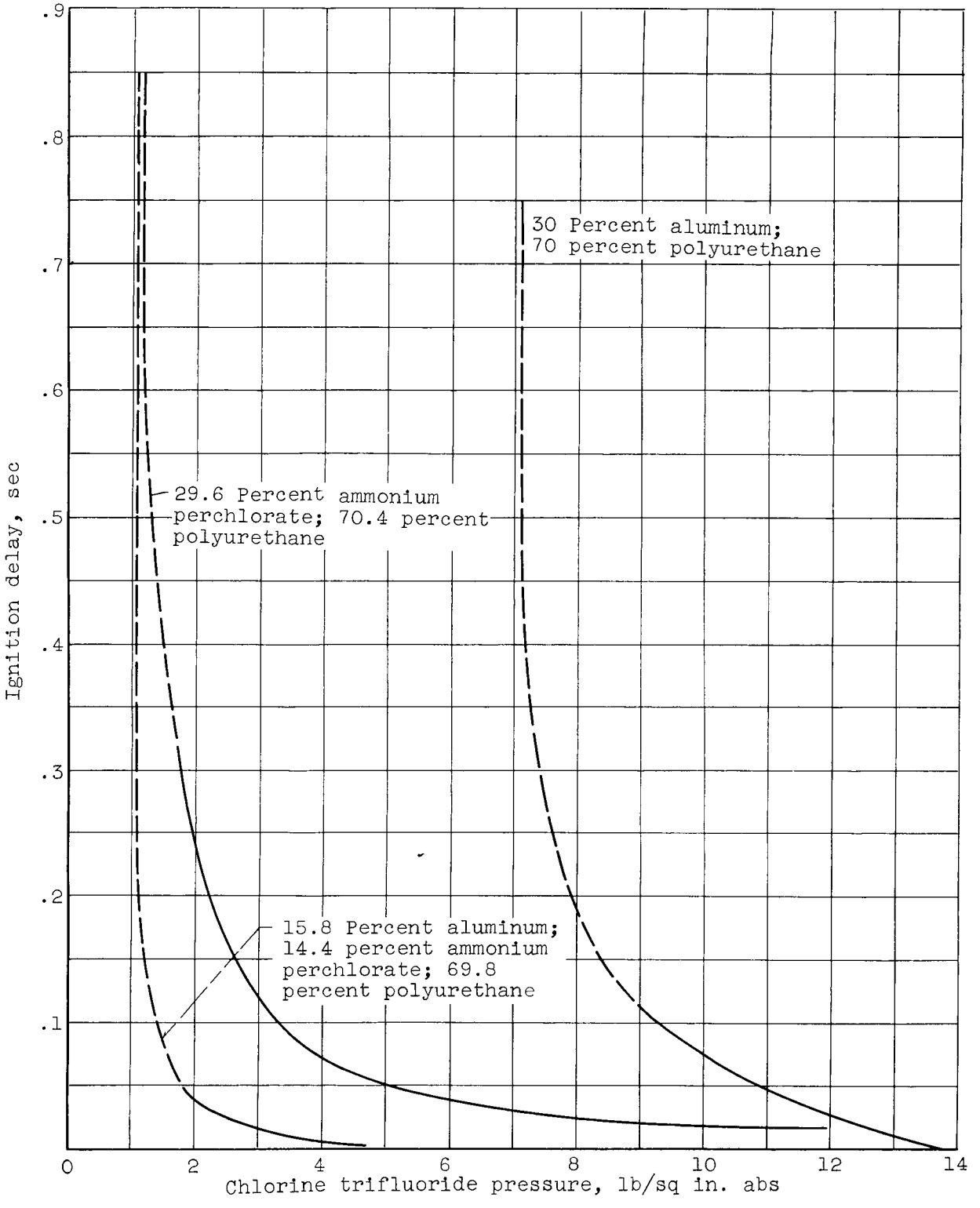
(d) Effect of aluminum addition to polyurethane binder.

Figure 3. - Continued. Ignition delay.



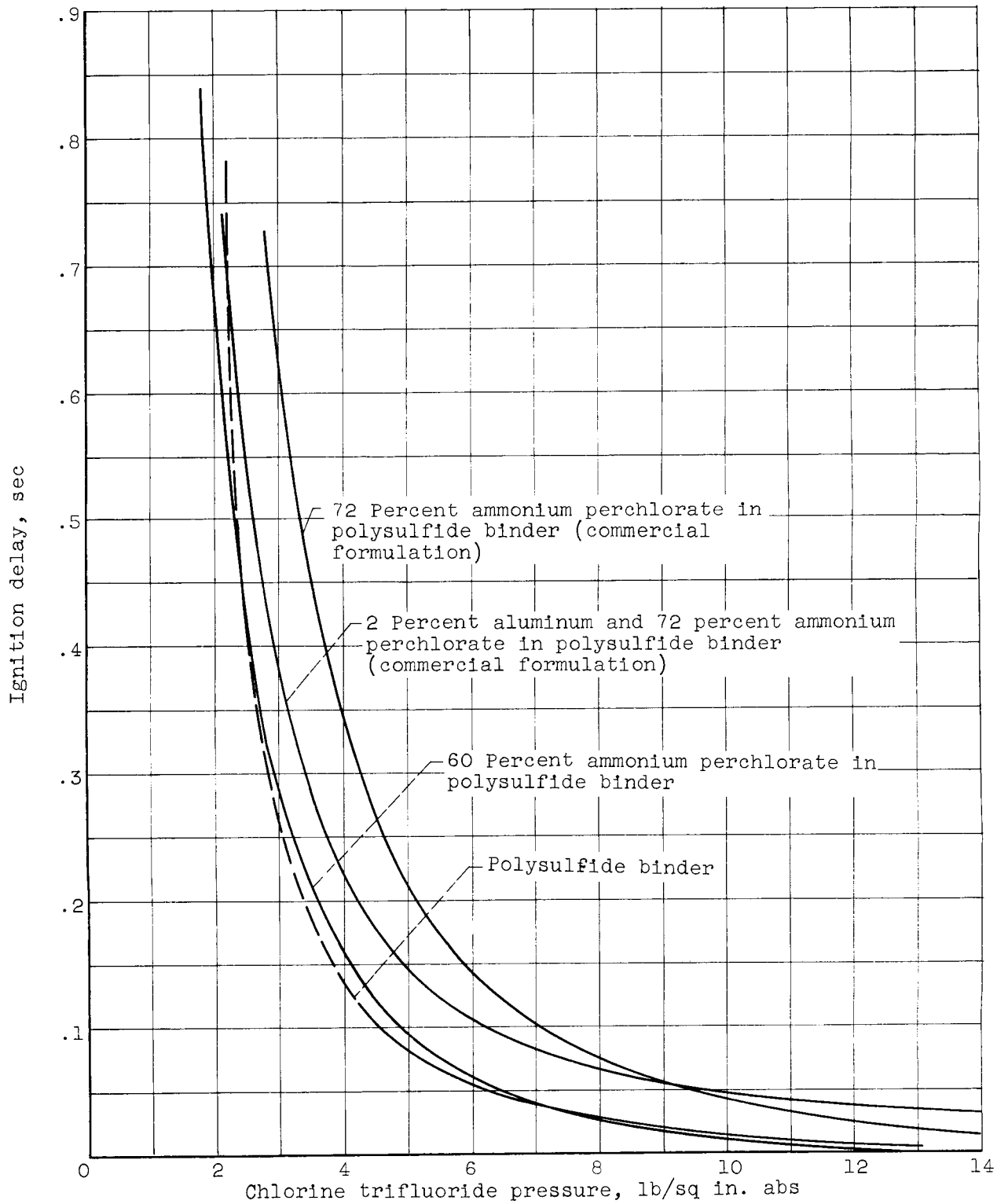
(e) Effect of aluminum addition to polyurethane propellant.

Figure 3. - Continued. Ignition delay.



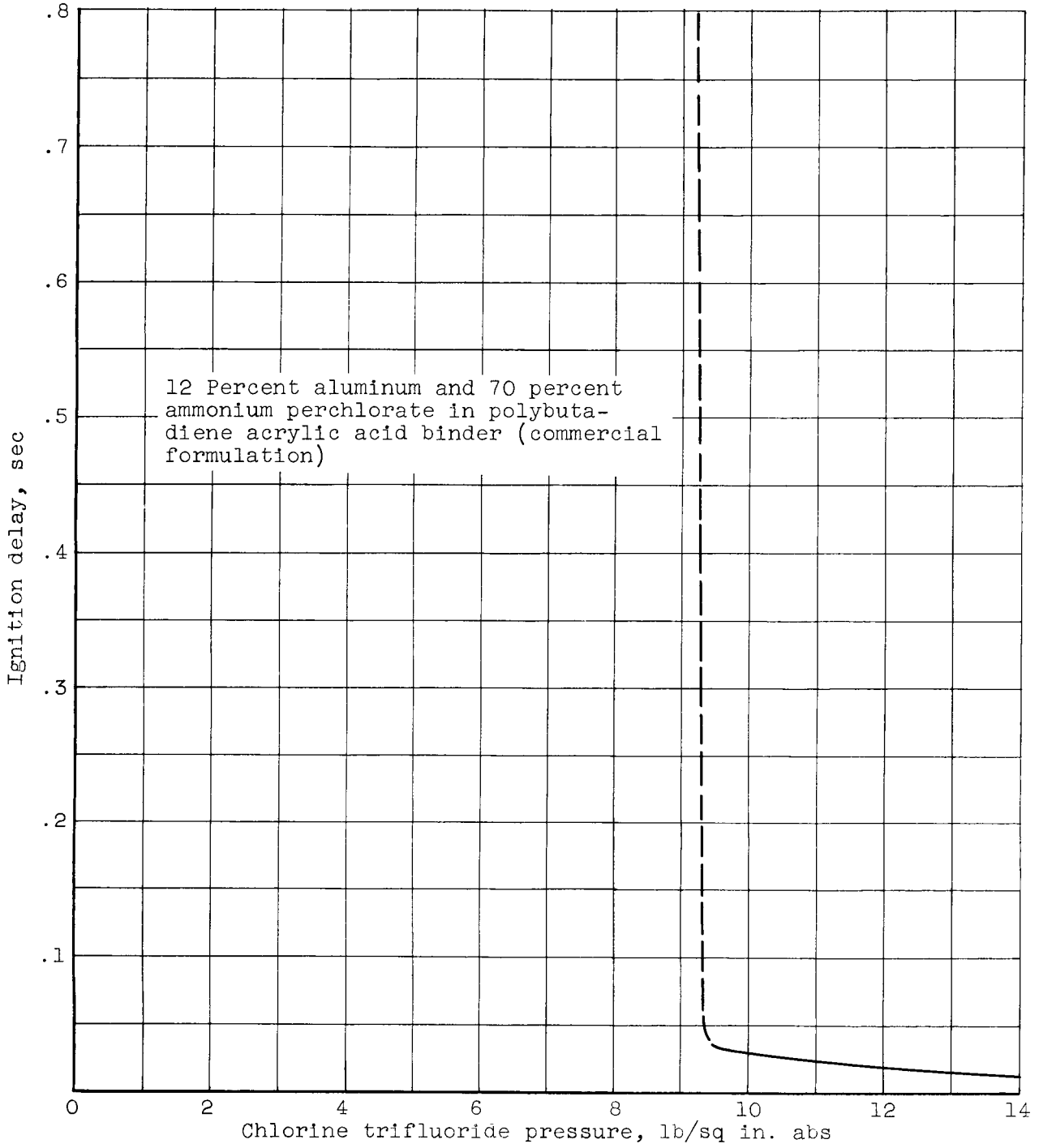
(f) Effect of equal binder surface area on polyurethane propellants.

Figure 3. - Continued. Ignition delay.



(g) Polysulfide propellants.

Figure 3. - Continued. Ignition delay.



(h) Polybutadiene acrylic acid propellant.

Figure 3. - Concluded. Ignition delay.